Synthesis and Characterization of

Gd based Manganese oxide

A thesis submitted in the partial fulfillment of the requirement for the degree of

MASTER OF SCIENCE

IN PHYSICS

BY

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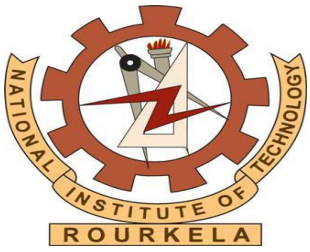
Under guidance
of
Dr. Suryanarayan Dash



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CERTIFICATE

This is to certify that the thesis about "**Synthesis and characterization of Gd based Manganese oxide**" being submitted by **Shanu Meena** to the Department of Physics & Astronomy, National Institute of Technology, Rourkela, Orissa, for, the degree of master of science is a record of genuine research carried out by her under my supervision and guidance.

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ACKNOWLEDGEMENT

On the submission of my thesis report titled **"Synthesis and characterization of Gd based Manganese oxide",** I would like to convey my gratefulness and sincere thanks to my supervisor Dr. Suryanarayan Dash, Department of Physics for his constant inspiration and support during the course of my work in the last two years. And I would like to express my greatest and sincere gratitude to research scholars of my lab, Lakshmana Rao Tangi and Nilakantha Tripathy; certainly without their kindness, guidance and great help, I would not have been able to complete this project thesis. And I would also like to thank all my friends for their support and help during my project.

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ABSTRACT

In this project, we investigate the details of the structure and morphology (XRD, UV-visible spectroscopy, FESEM) of $Gd_{0.5}$ $Sr_{0.5}MnO_3$. The sample is synthesized by wet chemical method, known as sol-gel process. The information about molecular bonding and structure is obtained from the x-ray diffractions. We also study its band gap properties from UV-Visible spectroscopy and the morphology of the material through FESEM.

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CHAPTER-1

INTRODUCTION

1.1: Multiferroic Material

A material that exhibits two or more primary ferroic properties such as ferromagnetism, ferroelectricity and ferroelasticity or ferrotoroidicity is described as a multiferroic.

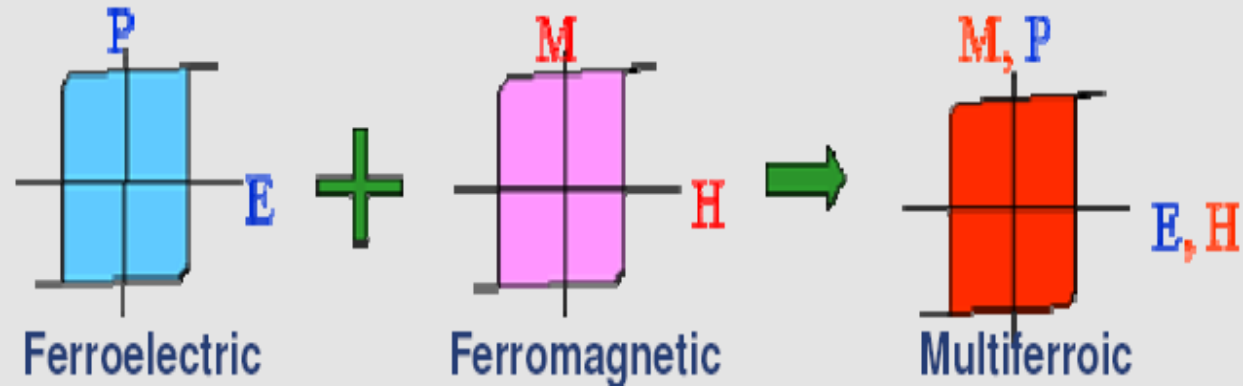


Fig 1: Multiferroics

ME coupling (Magnetoelectric coupling)

ME coupling is a process in which ferroelectric and ferromagnetism are coupled with each other so that multiferroic property should be achieved.

Application of Multiferroic Material:-

Piezo actuators, piezo sensor, ultra sound sensors, FE devices, FM devices, Ferroelasticity. Basically multiferroics is used to design smarter multiferroic material and to control their functionality for practical application. [1]

Types of Multiferroic:-

1. Type-I multiferroics
2. Type-II multiferroics

Type-I multiferroics:-

1. Weak coupling of ferroelectricity and magnetism.
2. Ferroelectricity at higher T then magnetism.
3. Large polarization.

Type-II multiferroics:-

1. Strong coupling
2. Ferroelectricity in low temperature
3. Weak polarization

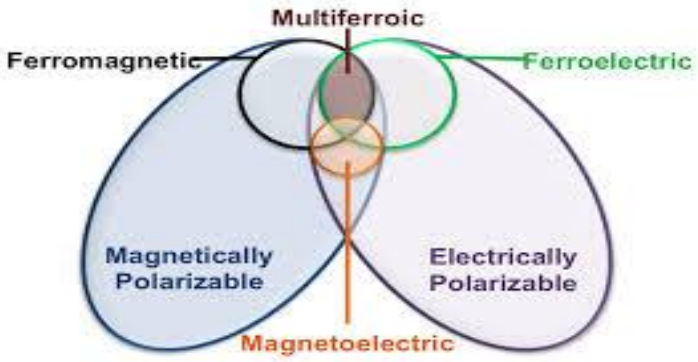


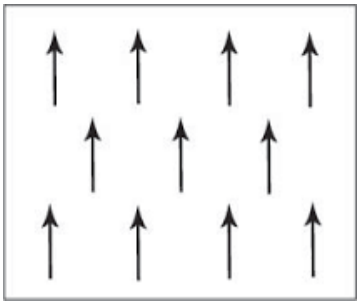
Fig 2: Magnetoelectric coupling.

Ferroic order in Materials

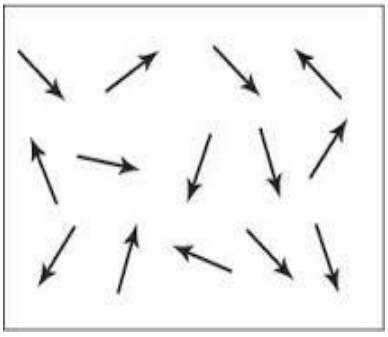
Material which have a spontaneous, switchable internal alignment termed as ferroic order.

1.2: Ferromagnets

Ferromagnetic material has spontaneous magnetization that can be switched by an applied magnetic field. A ferromagnetic material during a phase transition from a high-temperature phase that does not have a macroscopic magnetic moment to a low-temperature phase that has a spontaneous magnetization even in the absence of an applied magnetic field. Ferromagnetic material having magnetic flux density so its uses in transformer cores, permanent magnet and electromagnets basically ferromagnets have strong magnetic field. [3]



(ferromagnet)



(paramagnet)

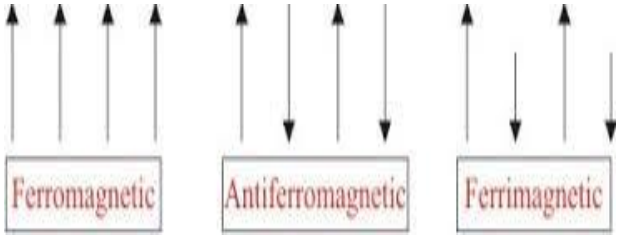


Fig 3: Ordering of the magnetic dipoles in magnetic material.

Hysteresis loop for ferromagnetic material:

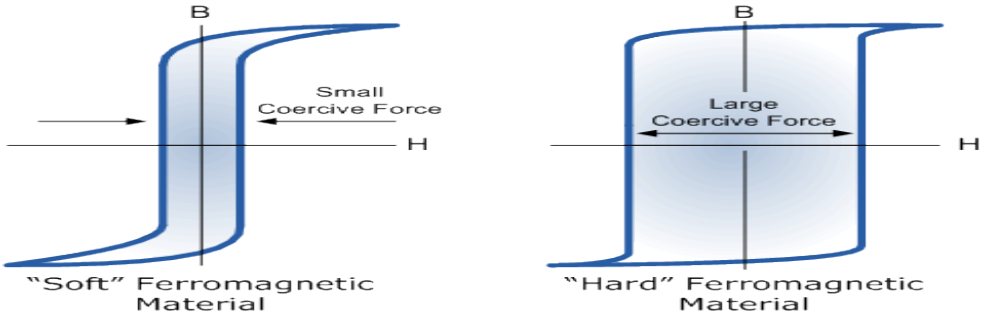


Fig 4 : Hysteresis loop for ferromagnetic material

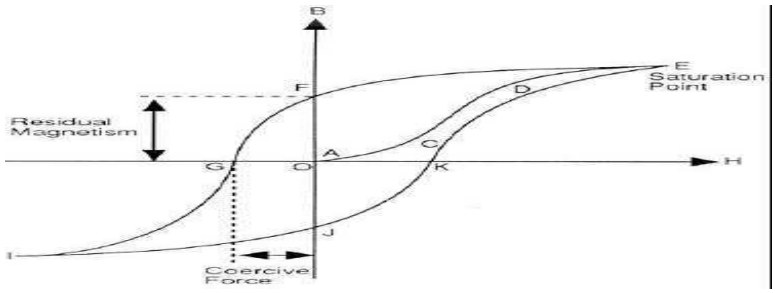


Fig 5: Hysteresis loop for ferromagnetic material

When magnetic field increases in positive direction then magnetic induction increases from zero to saturation point when magnetic field reduced to zero then induction is also reduced to zero this is called coercivity same process for negative direction. [3]

1.3: Ferroelectrics

These materials have spontaneous polarization that can be switched by an applied electric field. ferroelectrics material during phase transition from high-temperature phase that have a ordinary dielectric to a low-temperature phase that has spontaneous polarization in the absence of electric field. Various properties of ferroelectric materials are comparable to those of ferromagnets, but with the electric polarization P, corresponding to the magnetization M; The electric field E; And the magnetic field H; Similarly electric displacement D; and the magnetic flux density B. Ferroelectric materials also have domains and show a hysteric response of both polarization and electric displacement to an applied electric field as a result, they also find application in data storage. [4]

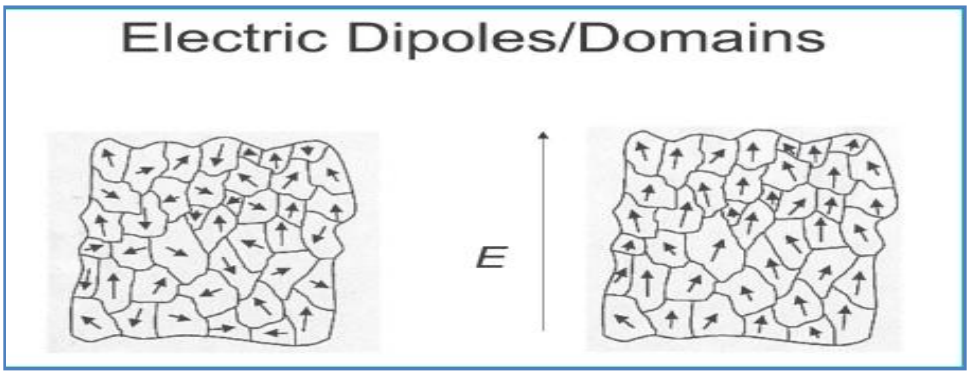


Fig 6: Electric dipole/ Domains

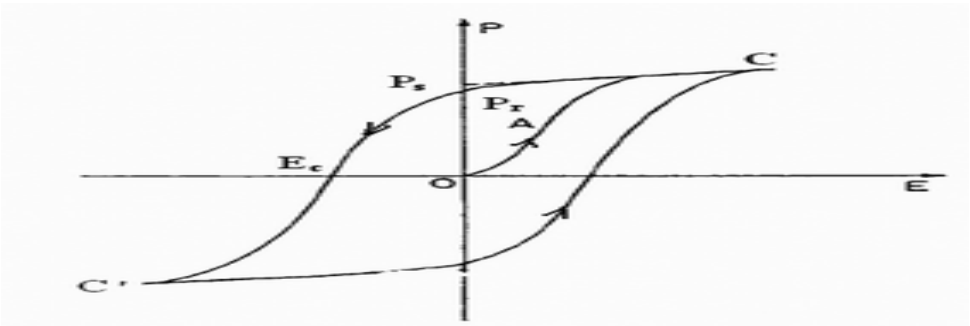


Fig 7: Hysteresis loop for ferroelectric material

Ferroelastic materials

Materials with spontaneous deformation that can be switched by an applied stress.

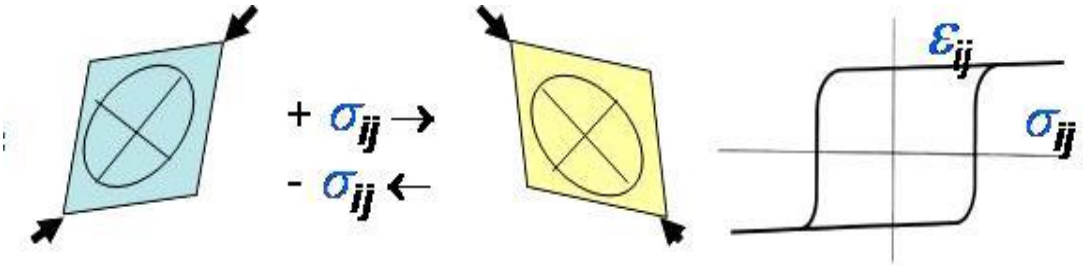


Fig 8: Hysteresis loop for ferroelastic material

1.4: Perovskites structure

The Perovskite compounds generally have the chemical formula like ABX_3. Here A and B represent cations of different sizes and X denotes the anion which binds with both A and B. Generally the A atoms are bigger in size than B atoms. The B cation has an ideal cubic symmetry structure and has a 6 fold coordination. It is surrounded by octahedral anions. Cation A has 12 fold octahedral coordination. For attaining stability, it depends solely on the ion size. A little buckle and bending can create lower symmetry distorted version in which coordination number of A and B, or of both are varied or reduced. [5]

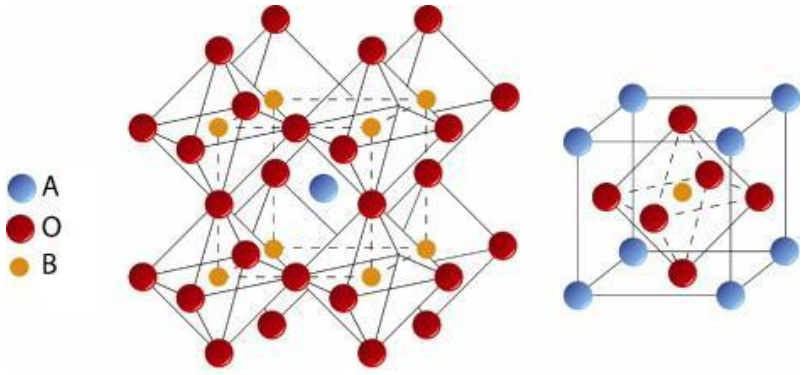


Fig 9: Cubic Perovskite structure.

The Perovskite structure is shown in the above figure, by oxides which have the chemical formula of ABO_3. In these type of compounds, the A atom fits at corner position of cube where as B atom fits body centered position of cube. An oxygen atom is there at the face centered position.. The stability of the structure, depends mainly on the ion size, if there will be small buckle or some bending, then that can create distort version of symmetry in which coordination of A and B are varied.[6]

1.7 Aim of the present work:-

We analyze the structural and optical properties of the doped compound and the properties of this compound will depend upon the interaction between the rare earth material and dopants. Structural analysis of the compound has been done by X-ray diffraction and was fitted to the theoretical data by Rietveld analysis. From the XRD pattern we analyzed pbnm and stoichiometrric of the sample. From the UV-VIS spectra, band gap of the sample was calculated. FESEM studies were done to see the microstructure and its grain size was calculated.

CHAPTER:2

SAMPLE PREAPARATION

2.1 Wet Chemical Method

This sample is prepared by wet chemical method. This method is the best synthesis methods for sample preparation because in this method we get the homogeneity in the sample and this method requires very low sintering temperature and also less polluted method. In this method mixing of molecules of the compound is very good. Sol-gel is the wet chemical method.

2.1.1 Sol-gel Process

Sol-gel is the process in which we get nanometric sized compound. Basically two things are required for this process one is solute and second is solvent. When polymer or colloidal particles immersed in solvent then sol is formed. After sol formation it heated with low temperature around 200oc. And addition of fuels is required in is process for accelerating the reaction. The solution stirred and heated at 70oc before adding fuel. Few reaction needs adjust the PH because we can identify sample is acidic or basic. Adjusting the PH value of the solution around 6-7 and solution continuously heated upto gel is not formed after gel formation, the solution is continuously heated up to all the gel of solution is burned and convert into black floppy and dried mass is formed. This is sol-gel transition or sol-gel process. Gels are basically classified into two categories, one is physical gel and other is chemical gels. The physical gels are related with the Vander Wall bond and hydrogen bond. This process is better than others because of its exclusive characteristics like require low temperature for sample preparation, less contamination, less wastage of sample and molecules of the compound mixed in best way. In this process the concentration, temperature and pH control is very important.[7]

2.1.2 Calcination

Calcinations is the first heat treatment process for the phase formation. In this treatment the solid sample is heated below its melting point and it is also carried out inside the furnace with high temperature or low temperature. During calcinations process the impurities and ingredient are removed from the sample due to oxidation. Initially the grinded powder is placed inside a

furnace, then heating the powder with a control manner for few hours basically inside the furnace temperature must be in controlled manner. If the temperature is not increase in controlled manner then sample will damage inside the furnace. If the sample is directly contact with high temperature then chances of splitting of sample inside the furnace so temperature increase in controlled manner. During this treatment the sample molecules arrange themselves in a homogeneous manner or in a particular order. After the calcinations of the sample we can easily made pellet for sintering.

2.1.3 Palletisation

Palletisation means to make the pellets with the help of patizer and die set. The sample is calcined in homogeneity nature, initially the sample will put into a die set and applying pressure to the head of the die set. Due to this high pressure the particles of powders are packed close to each other and compact strongly to each other. For palletisation no specific pressure for a particular compound.

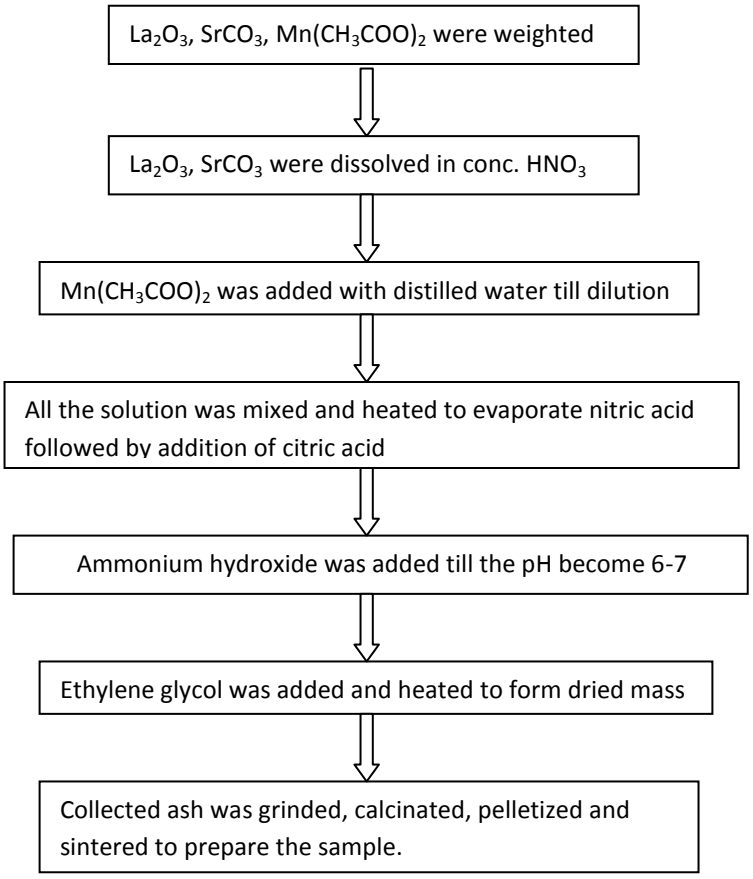
But mostly the superconducting materials require high pressure for the pellet formation. But perovskite and double perovskite require low pressure for pallet formation. In this process the particles are closely packed to each other by high or low pressure with decreasing the densification. Sometimes binder is used for palletisation for the strength.[8]

2.1.4 Sintering

Sintering is the heat treatment process for the phase formation. After formation of pellet, it was again heated with suitable temperature and also with a controlled manner. Aft heating bonding between the particles of the sample leads to coherent, predominately. Basically heating increase the bonding strength of the pellet. After calcinations sintering is take place basically sintering process is depends on the temperature and time ratio. The temperature should be in controlled manner with respect to time and the temperature should be below then the melting temperature. If the temperature more than the melting temperature then there is chances of phase lost and sample may be damage if temperature more than melting temperature.[9]

2.3 Sample preparation

This sample is prepared by sol-gel method. The detail process for the preparation for the sample is given in the following by flowchart.



Experiments Details

The polycrystalline sample $Gd_{0.5}Sr_{0.5}MnO_3$ is prepared by wet solid state reaction method. In this method initially stoichiometry amount Gd_2O_3,$SrCO_3$,MnO_2 were mixed in conc. HNO_3 then the solution was heated, boiling off the HNO_3 after heating solution was calcinated in air at 900^0C overnight. After calination dried mass is formed then this black powder was pressed into pallets and sintered at 1200^0C in air for 12 hours. Then sample was analyzed by XRD,UV-visible spectroscopy and FESEM.

CHAPTER:3

CHARACTERIZATION TECHNIQUES

3.1 X-ray Diffraction:-

It is one of the best methods for characterization of sample and this method gives information about structure of crystal and composition of crystal and about the lattice parameter and also gives information about the spacing between the planes of crystal.XRD method is a very main and common technique in order to portray the materials and to learn the structural clarification in particulars. The determination of structure of crystal is very significant since most of the bodily properties like ferroelectric, optical, magnetic properties depend upon the array of atoms in sample. XRD pattern are usually used to found the collection of material or atomic collection because of the d-spacing in diffraction planes is some order of x-ray wavelength.

When high energetic beam of X-ray incident on the sample and X-ray also diffracted, it can go to very deep into sample and thus can give many useful data about the crystal structure of the sample. The collide between a X-ray photon and atom of the sample, then some of photon deflect away from their original path of travelling. When the scattering is calculated to be elastic, only there will be modify in momentum and won't be any vary of energy or wavelength. After the transfer of momentum from photon of X-ray to atom of sample, the diffracted X-ray will give the information about the distribution of atoms in the lattice.[10]

The XRD peak and the d-spacing are openly related to each other by the formula which is known as the Bragg's law.XRD basically based on Bragg's law.

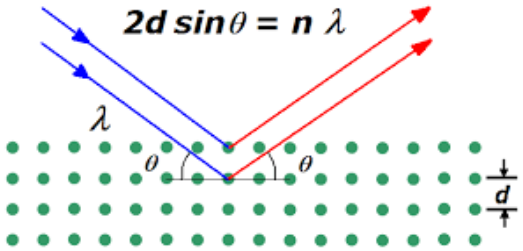


Fig 11: X-Ray diffraction through crystal planes

$$2d\sin\theta = n\lambda$$

Where symbols have their usual meanings

The Rietveld analysis which was calculated to portray the properties of crystalline materials was urbanized by Hugo Rietveld. There occur some peaks in intensity in diffraction pattern at certain location when the sample is characterized by x-ray diffraction. Many properties of materials can be determined by the using of these peaks' height, position and width. This route includes using of a most square move toward to purify theoretical line outline till it matches with the experimental profile. It was specially calculated to deal with the peaks which are powerfully overlapped.[11]

3.2 FESEM (Field Emission Scanning Electron Microscope)

The FESEM method is used to study the morphological arrangement and compositional analysis of the substance. But it could not be able to give improved resolution since the application of field emission in the electron gun of the FESEM has thinner probing having high electron energy. As a consequence the resolution is 3-6 times better than the SEM. It also benefits in minimizing the sample damage. In the FESEM we obtain the grain boundaries in nanometric range. [12]

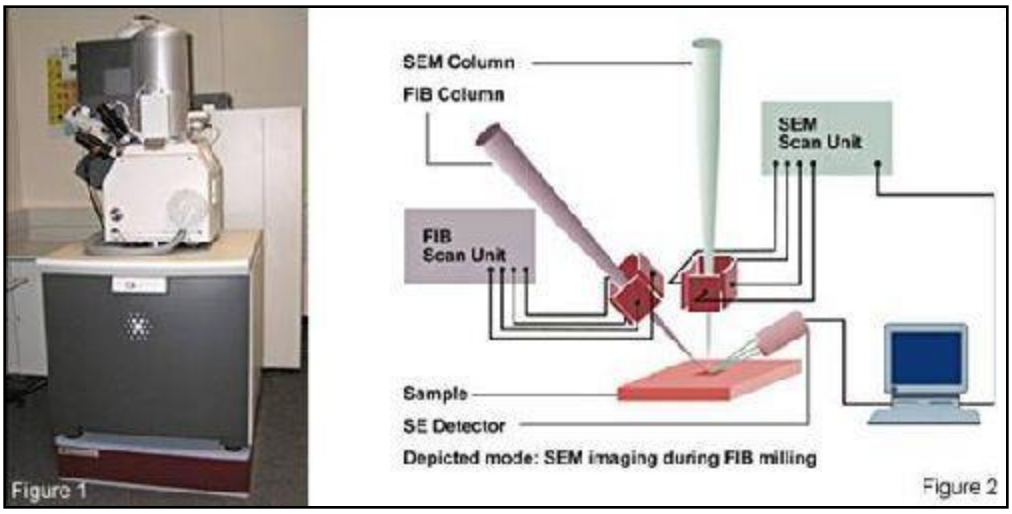


Fig 12: Schematic diagram of FESEM

UV-Visible Spectroscopy

UV-visibility spectroscopy denotes that the absorbance or reflectance obtained in the visible spectral regime. Transition between electromagnetic spectra and molecules is obtained. As a result the electrons are exited from ground to exited state. When these excitation rates are high, the spectra of larger wavelength are seen in visible regime. It is used for characterization for distinct substance like transition metal ions, organic and biological organics. This method is utilized for finding the band bap of the sample. As a consequence the conductivity of the sample is found with ease. [13]

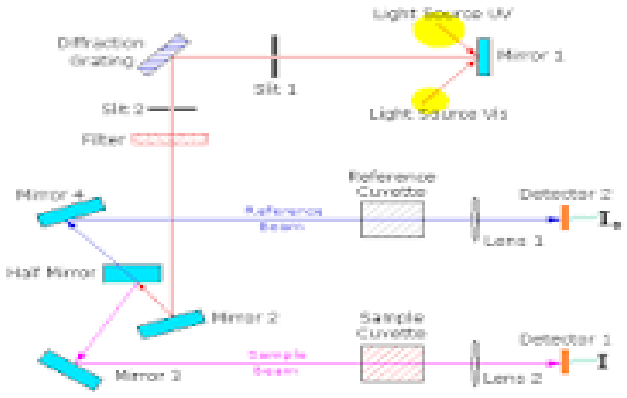


Fig 13: Schematic diagram of UV-visible spectra

CHAPTER: 4

RESULT AND DISCUSSION

4.1: Structure Determination by XRD

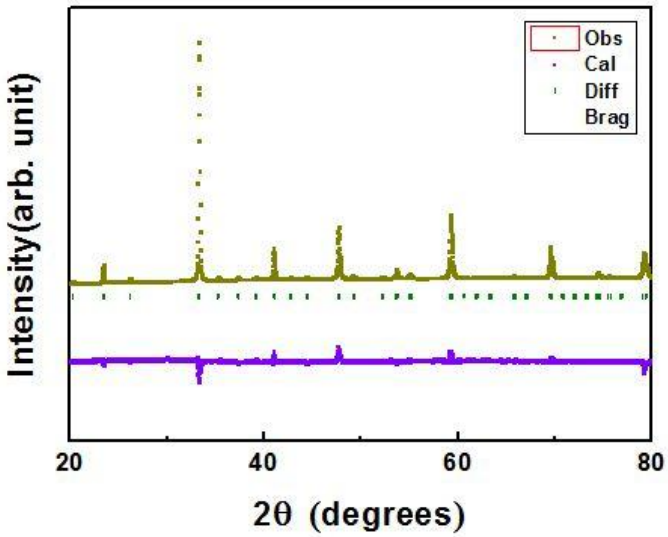


Fig 14: (XRD pattern of $Gd_{0.5}Sr_{0.5}MnO_3$)

The above figure represents the XRD data and Rietveld analysis of $Gd_{0.5}Sr_{0.5}MnO_3$. From this we can see the samples are in single single phase orthorhombic structure with space group pbnm. For the sample, we have used the parameter,

Parameters	Gd	Sr	Mn	O_1	O_2
X	-0.00457(19)	-0.00457(19)	0.0000	1.0726(10)	1.2205(12)
Y	0.0224(6)	0.0224(6)	0.5000	-0.2143(62)	2.7901(10)
Z	0.2500	0.2500	0.0000	0.2500	0.0038(6)

Cell parameters	a(Å)	b (Å)	c(Å)	Volume(Å)^3
	5.4191(26)	5.4253(2)	7.6493(3)	224.8912

4.2: Band Gap study by UV-visible Spectroscopy:-

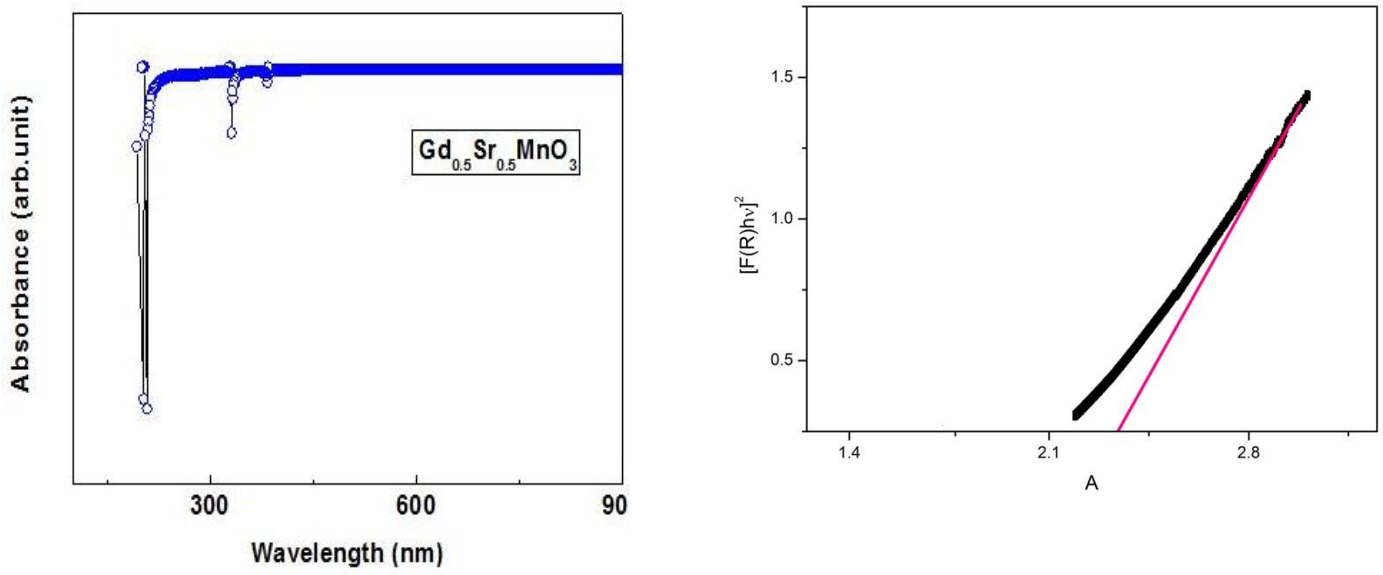


Fig 15(a): (UV-visible spectra of $Gd_{0.5}Sr_{0.5}MnO_3$) **(b)** (Band gap of $Gd_{0.5}Sr_{0.5}MnO_3$)

The above two figures represents the UV vis absorption spectra for $Gd_{0.5}Sr_{0.5}MnO_3$. The direct band gap energy was determined by fitting absorption data to direct transition equation $(h\nu F(R))^2=A(h\nu-E_g)$. The extrapolation of linear portion of curve towards absorption gives E_g for direct transition. The value is found to be 1.9eV. this shows the semiconductive property of the sample.

4.3: Microstructure by FESEM:-

FESEM determine the size and composition of the material (sample). The average particle size of the sample found to be around 479.3nm in the form of pallet at 1200^0C.

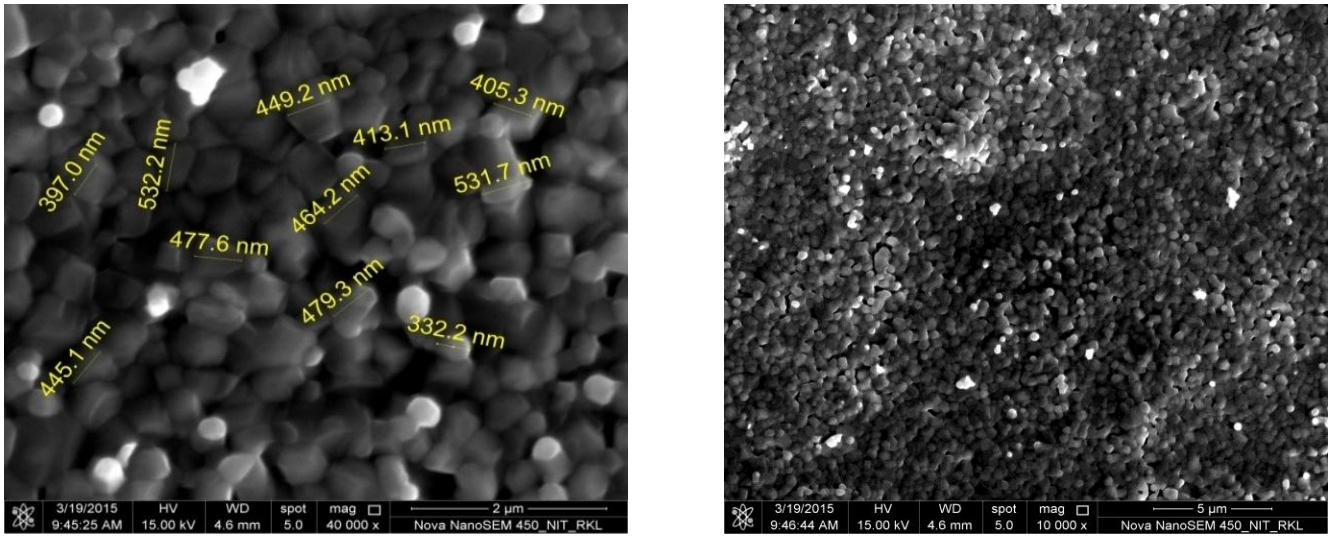


Fig 16: (FESEM Micrograph of $Gd_{0.5}Sr_{0.5}MnO_3$ in different Scale indicating grain size.)

CHAPTER: 5

CONCLUSION AND SCOPE OF FUTURE WORK

We studied the detailed structural images, and band gap. The sample is prepared by Sol-gel technique. The structural analysis of sample is carried out by detailed Rietveld analysis of XRD data which shows that the sample is in a single phase. The sizes and granular information are probed by FESEM study. The band gap of the sample is measured by UV VIS spectroscopy technique which proves that these are by nature, semiconducting.

Furthermore, we can study the dielectric and magnetic properties and correlation between electric and magnetic order parameter of the sample.

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